Co-evolution of atmospheres, life, and climate

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Co-Evolution of Atmospheres, Life, and Climate

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Abstract

After Earth's origin, our host star, the Sun, was shining 20–25% less brightly than today. Without greenhouse-like conditions to warm the atmosphere, our early planet would have been an ice ball, and life may never have evolved. But life did evolve, which indicates that greenhouse gases must have been present on early Earth to warm the planet. Evidence from the geological record indicates an abundance of the greenhouse gas CO_2. CH_4 was probably present as well; and, in this regard, methanogenic bacteria, which belong to a diverse group of anaerobic prokaryotes that ferment CO_2 plus H_2 to CH_4, may have contributed to modification of the early atmosphere. Molecular oxygen was not present, as is indicated by the study of rocks from that era, which contain iron carbonate rather than iron oxide. Multicellular organisms originated as cells within colonies that became increasingly specialized. The development of photosynthesis allowed the Sun's energy to be harvested directly by life-forms. The resultant oxygen accumulated in the atmosphere and formed the ozone layer in the upper atmosphere. Aided by the absorption of harmful UV radiation in the ozone layer, life colonized Earth's surface. Our own planet is a very good example of how life-forms modified the atmosphere over the planets' lifetime. We show that these facts have to be taken into account when we discover and characterize atmospheres of Earth-like exoplanets. If life has originated and evolved on a planet, then it should be expected that a strong co-evolution occurred between life and the atmosphere, the result of which is the planet's climate. Key Words: Early Earth—Biomarker—Atmospheres—Climate—Exoplanets. Astrobiology 10, 77–88.

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1. How Life Has Affected Earth's Atmosphere

To estimate the occurrence of terrestrial exoplanets and maximize the chance of finding them, it is crucial to understand the formation of planetary systems in general and of terrestrial planets in particular. A reliable formation theory should not only explain the Solar System, with small terrestrial planets within a few AU and gas giants farther out, but also the newly discovered planetary systems with close-in giant planets. Regarding the presently known exoplanets, it should be stressed that our current knowledge is strongly dependent upon the sensitivity limits of the current detection techniques (mainly the radial velocity method). With time and improved detection methods, the diversity of planets and orbits in exoplanetary systems will definitely increase and help to constrain the formation theory further.

Nitrogen on Earth was outgassed during the first hundred million years. Therefore, the atmospheric pressure was at least 0.8 bar in Earth's prebiotic atmosphere. If climate regulation via the carbonate-silicate cycle is assumed (Walker, 1977; Walker *et al.,* 1981), then the level of CO_2 is determined to a first approximation by the solar luminosity.

- Due to the faint luminosity of the early Sun (*e.g.,* Gough, 1981; Baraffe *et al.,* 1998), about 200–300 mbar of CO_2 would have been necessary to ensure a mean surface temperature above 273 K (Kasting *et al.,* 1993).

Molecular hydrogen was likely the third main component of Earth's prebiotic atmosphere; in an enhanced presence of CO_2 and if large amounts of hydrogen were absent in the upper atmosphere, the exosphere may have been relatively cool, which could have resulted in low escape rates of atomic hydrogen (Tian *et al.,* 2005). Hydrogen that was released by volcanoes but not efficiently lost to space must have accumulated to levels of the order of 200 mbar (Tian *et al.,* 2005). As water was present on Earth before 4.4 Gyr, water vapor was also an important constituent of the lower atmosphere. Other atmospheric species that may have been present at this time include CO and sulfur-bearing species like H_2S released by volcanoes and possibly methane produced abiotically in hydrothermal vents.

1.1. A rise in methane?

Among the most primitive archaea found in the tree of life, as shown in Fig. 1, are the methanogens, some of which are autotrophic (consuming CO_2 and H_2) and others heterotrophic (consuming organic molecules). Methane is a trace gas in the present Earth atmosphere (about 2 ppm), and its origin is biological except for a small fraction produced in hydrothermal systems.

- Methanogens existed almost certainly during the Archean and the Neoproterozoic, when the atmosphere was still anoxic (before 2.3 Gyr).

If we assume a biogenic release equal to the present day, the level of methane would have reached 100–1000 present atmospheric level (PAL) in the absence of atmospheric O_2 (Pavlov *et al.,* 2000). As today's methanogens can only grow in very limited environments where O_2 is absent and H_2 or organics are present, the production of methane by the biosphere was probably much higher in the early anaerobic environment. Thus, very high levels of methane can be inferred, which lasted for more than 1 Gyr, between the emergence of methanogens (probably earlier than 3.4 Gyr) and the rise of O_2 (2.3 Gyr).

- Such high levels of CH_4 would have had a strong impact on climate and geochemical cycles. Methane is a very efficient greenhouse gas, and levels higher than 100 PAL would potentially have been enough to warm the surface above 0°C (Pavlov *et al.,* 2000), which implies that climate is no longer regulated by the carbonate-silicate cycle. The level of CO_2 could potentially have been extremely low if methane became the main greenhouse gas, and this seems to be confirmed by the studies of paleosols from the Late Archean and Neoproterozoic, in which no trace of carbonates were found (Rye *et al.,* 1995; Hessler *et al.,* 2004). Note that this does not take the effect of hazes into account. In the early atmosphere, the haze expected from CH_4 photolysis was probably weak if the CH_4/CO_2 ratio did not exceed unity. If the ratio had exceeded unity, an organic haze would have formed (Pavlov *et al.,* 2003) such that it would have potentially cooled the atmosphere and regulated the greenhouse effect. Another important consequence of high levels of CH_4 is the transport of hydrogen, which would have dissociated from methane by high extreme UV radiation of the young Sun to the upper atmosphere and led to a much higher escape rate of hydrogen to space.

Thus, it might be possible that biological methanogens contributed to the oxidation of the atmosphere and lithosphere and enhanced the loss of H, making possible, later, the rise of oxygen (Catling *et al.,* 2001).

1.2. The buildup of O_2

Geological records have revealed the chemical action of free oxygen after about 2.3 Gyr ago (Bekker *et al.,* 2004), except for some deposits from the deep ocean that remained anoxic for a few hundred million years or more (Rouxel *et al.,* 2005).

- It seems that the buildup of atmospheric O_2 occurred at least 400 Myr after the emergence of oxygen-producing bacteria capable of oxygenic photosynthesis (Fig. 2).

Indeed, 2.7 Gyr old molecular fossils are interpreted as the remains of primitive cyanobacteria and eukaryotes, which are producers and consumers of O_2, respectively (Brocks *et al.,* 1999). Several reasons could explain this delay. First, the budget reaction of oxygenic photosynthesis also works in the reverse direction, since respiration and oxidation of organic sediments consume oxygen.

- Thus, the buildup of atmospheric O_2 requires the burial of the organics produced by photosynthesis.

This occurs today at a rate of 589 Tg O_2/year (Catling and Claire, 2005), which means that the net release of the present O_2 atmospheric content (10^{21} g O_2) takes about 2 Myr (this is about 1000 times slower than the production of O_2 by photosynthesis). This rate is balanced by the oxidation of rocks, old sediments, and volcanic gases. The oxidation sinks for O_2 may have been much more efficient on early Earth, partly

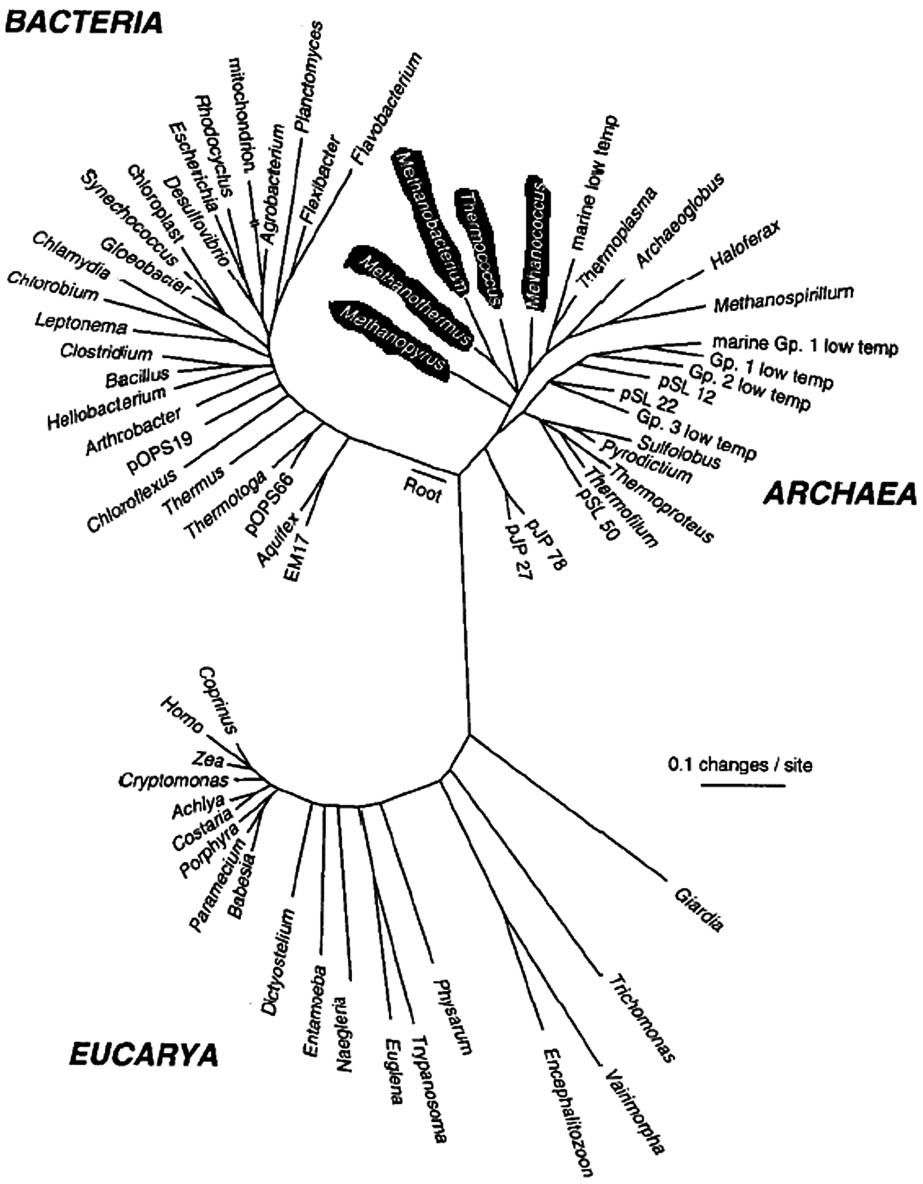

FIG. 1. Tree of life: in black are indicated some methanogens that are among the most primitive life-forms known (courtesy of N. Pace).

due to the presence of large amounts of reduced iron in the ocean and the crust (Walker, 1977).

- In the absence of efficient organic burial, O_2 would not build up.

Some tectonic processes may have favored the burial of reduced carbon and allowed the rise of O_2 by about 2 Gyr ago (Des Marais *et al.*, 1993). Another hypothesis has already been mentioned and is linked with the slow oxidation of Earth through the escape of hydrogen to space: in other words,

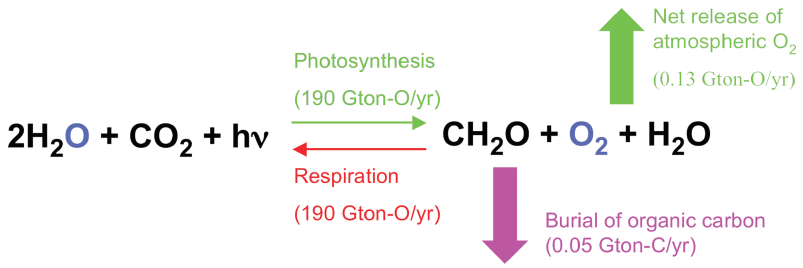

FIG. 2. Illustration of reactions that result in a release of O_2 in Earth's atmosphere. Color images available online at www.liebertonline.com/ast.

- the Earth had to be depleted of a lot of hydrogen before an oxygen atmosphere could occur.

There might also be a climatic reason for the delay between the emergence of O_2 producers and the rise of O_2. CH_4 has a very short photochemical lifetime in an O_2-rich atmosphere, which means that a consequence of a buildup of O_2 is a decrease of the CH_4 atmospheric abundance and, thus, a fall of the mean surface temperature that could lead to a global freezing event.

Therefore, in a biosphere where CH_4 and O_2 producers both exist, the solar luminosity might be a strong constraint on the timing of the oxygenation (Selsis, 2002).

- All these constraints on the buildup of an O_2-rich atmosphere are extremely important for astrobiological considerations, as some authors argue that complex multicellular life can only develop in an oxic environment (*e.g.,* Catling *et al.,* 2005).

Geological records have provided us with only qualitative information about the presence or absence of oxygen in the atmosphere. After the rise of O_2 and until the end of the Precambrian (about 550 Myr ago), it can only be inferred that the level of O_2 was above about 1% PAL (0.2% in abundance). Models based on the chemical and isotopic composition of sedimentary rocks of the Phanerozoic (from 550 Myr ago to now) allow us to trace back the evolution of the level of O_2 and show that it has varied roughly between 0.7 and 1.8 PAL (Berner *et al.,* 2003).

- The highest oxygen level (nearly twice that of today, which implies an atmospheric pressure 15% higher) is found to have occurred during the Permo-Carboniferous.

The principal cause of this enhanced level was the rise of large vascular land plants and the consequent increased global burial of organic matter. Higher levels of O_2 are consistent with the presence of Permo-Carboniferous giant insects.

1.3. The rise of the ozone layer

Ozone (O_3) is produced by only one reaction: $O + O_2 + M \rightarrow O_3 + M$, where M is any compound (this is called a three-body or association reaction) and atomic oxygen comes from the photolysis of O_2. On the other hand, O_3 is destroyed by photolysis and many trace compounds in the atmosphere (HO_x, NO_x, ClO_x, …).

- Therefore, the amount of O_3 in the atmosphere depends on the level of O_2 but also on the abundance of these trace gases on which we do not have enough information to infer the level of O_3 in the Precambrian.

The variation of O_2 alone during the last 550 Myr would not have changed significantly the level of O_3, as O_3 has only a weak dependency on the O_2 level (Léger *et al.,* 1993; Segura *et al.,* 2003).

The abundance of O_3 was more certainly affected by changes in the content of trace gases. We do not know for sure whether, between the rise of O_2 and the beginning of the Phanerozoic, O_3 provided a UV shield for land life, but it can be inferred that it was present when the first lichens colonized the lands during the Ordovician (500–425 Myr ago).

2. Stellar Radiation and Climate: Implications for Atmospheric Biomarkers*

It is well known from satellite observations and the output of coupled chemistry-climate models on Earth that important physical factors like atmospheric temperature and solar radiation affect atmospheric biomarker molecule concentrations over diurnal and seasonal timescales.

- Since it is expected that a terrestrial exoplanet-finding mission will discover terrestrial exoplanets for various stellar spectral types and stellar evolution phases, how different radiation inputs and climate feedbacks can affect biomarker signals must be studied.

As a first step, changes to biomarkers in Earth's atmosphere in response to variations related to orbital parameters, climate feedbacks, and the radiation and particle environment of the Sun or stars or both can be studied with the use of theoretical climate models (Fig. 3).

2.1. Ozone (O_3)

Tropospheric O_3 makes up about 10% of the overhead column content in the terrestrial atmosphere. In the lower troposphere (0–8 km), O_3 is formed when volatile organic compounds such as CH_4 are oxidized in the presence of NO_x (see overview in Crutzen, 1988), and it is destroyed by surface deposition. In the mid- to upper troposphere (8–18 km), stratospheric-tropospheric exchange affects O_3 concentrations. Here, stratospheric air may fold down into the troposphere and release O_3-rich air. Stratospheric O_3 makes up about 90% of the O_3 layer that forms when O_2 is photolyzed (<242 nm) into O, which then reacts with O_2 to form O_3.

- Why does an O_3 layer form at a specific altitude?

In the lower atmosphere, there is little O_3 because UV radiation is weak; in the upper atmosphere, there is little O_3 because there is little O_2. Figure 4 shows that the trade-off between UV and O_2 availability with altitude leads to a sharply defined O_3 maximum in the tropical stratosphere at 10 mbar (30 km), which travels each year across the equator toward the summer hemisphere where photolysis rates are higher.

In the lower stratosphere (18–25 km, 100–50 mbar), chemical timescales that affect O_3 are long compared with dynamical timescales. Thus, O_3 behaves as a quasi-inert tracer of dynamical motion in that it is quasi-horizontal along isentropic (constant entropy) surfaces with typical stratospheric horizontal and vertical diffusion coefficients of 1000 and 0.015 $m^2\ s^{-1}$, respectively (*e.g.,* Waugh *et al.,* 1997).

In the upper stratosphere (35–45 km, 5–1 mbar), O_3 is controlled mainly by chemistry. The main source is $O_2 + O + M \rightarrow O_3 + M$, whereas important sinks are $O + O_3 \rightarrow 2O_2$ and $O_3 + h\nu$ (<320 nm) $\rightarrow O + O_2$. These reactions were first discussed in depth by Chapman (1930) and are usually referred to as Chapman chemistry.

- On Earth, O_3 is formed in the tropics via Chapman chemistry and is then transported slowly (over several months) to mid- and high latitudes.

*The term biomarker is used here to mean detectable atmospheric species or set of species whose presence at significant abundance strongly suggests a biological origin.

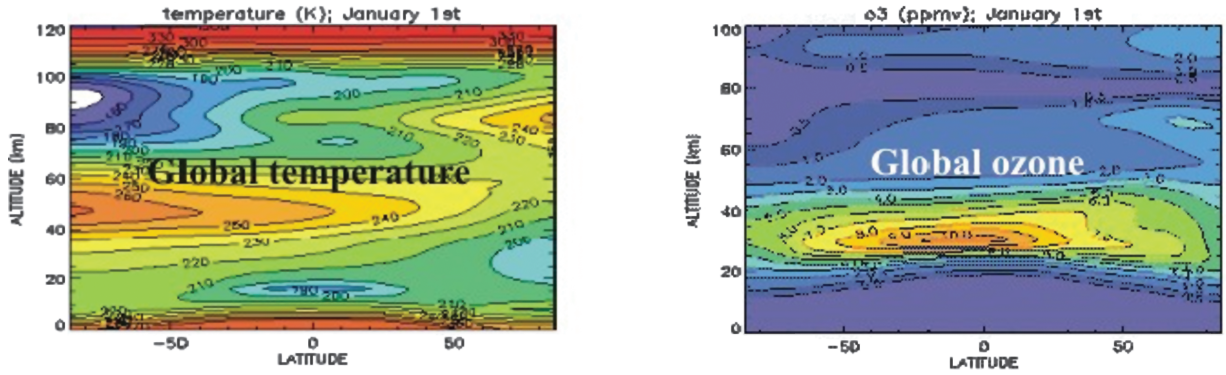

FIG. 3. Modelled zonal-mean temperature in Kelvin (**left**) and Ozone in parts per million by volume (**right**) for the Earth in January [the results were taken from the SOCRATES model at the Atmospheric Chemistry Division at the National Center for Atmospheric Research (Brasseuer, 1993)]. Color images available online at www.liebertonline.com/ast.

Chapman chemistry alone would produce more than twice as much O_3 as is measured. To explain the discrepancy, catalytic cycles that destroy O_3 were proposed:

$$X + O_3 \rightarrow XO + O_2$$
$$XO + O \rightarrow X + O_2$$
$$\text{Overall}: \quad O_3 + O \rightarrow 2O_2$$

where X can be OH (Bates and Nicolet, 1950), NO (Crutzen, 1970), and Cl (Molina and Rowland, 1974). The cycles are referred to as HO_x, NO_x, and ClO_x cycles. Stratospheric HO_x comes, for example, from H_2O degradation, NO_x from N_2O photolysis, and ClO_x from man-made chlorofluorocarbons. HO_x cycles are generally important in the tropical lower stratosphere, NO_x in the middle, and ClO_x in the upper stratosphere (*e.g.*, Lary, 1997, and references therein).

- Stratospheric O_3 features a natural cycle with around 20% more column O_3 in spring than in autumn.

The spring maximum is associated with less photolytic O_3 loss over the preceding winter. At polar latitudes, the natural cycle is opposed by the O_3 hole that forms via chemical processes in spring with typically 30–60% loss in the column. Over short timescales (days to weeks), the O_3 column in mid- to high latitudes is affected by atmospheric dynamics (Staehelin, 1998).

In the mesosphere (50–85 km), intense UV radiation leads to a diurnal cycle with daytime conversion of O_3 to O^3P. Observations by Zommerfelds *et al.* (1989) suggest a factor of 3 variation in O_3 at 65 km and a factor of 6 variation at 74 km. HO_x cycles are an important sink for mesospheric O_3 (Summers *et al.*, 1996).

2.2. Water (H_2O)

On Earth, the vast majority of atmospheric H_2O resides in the troposphere.

- The region around the tropopause acts as a cold trap that prevents most H_2O from reaching the stratosphere.

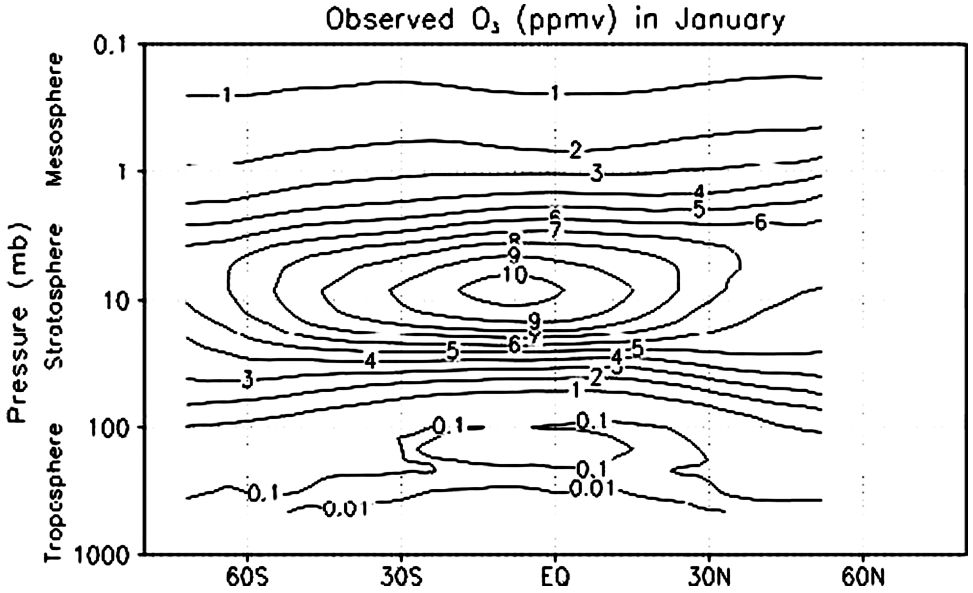

FIG. 4. Zonal-mean O_3 concentration (parts per million by volume) shown as a function of altitude. Data represent the mean of 11 Januaries from 1992 to 2002, data level 2 version 19 measured by the Halogen Occultation Experiment aboard the Upper Atmosphere Research Satellite (Russell *et al.*, 1993).

Figure 5 shows the H_2O concentration, as does Fig. 4 for O_3 as a function of zonal-mean height. Gettelman *et al.* (2000) reviewed processes that regulate the entry of H_2O from the troposphere into the stratosphere. Strong convective cloud events in the tropics achieve this if they penetrate the lower stratosphere. Methane oxidation is an important source of stratospheric H_2O and is initiated by reaction with hydroxyl (OH): $CH_4 + OH \rightarrow CH_3 + H_2O$.

Mesospheric H_2O features an annual cycle with amplitude of $\sim$20% and maximum in summer linked with stronger upward transport of damp air (Jackson *et al.*, 1998).

2.3. Methane (CH_4)

On Earth, between 80–90% of CH_4 resides in the troposphere, where it is well mixed. Figure 6 shows CH_4 concentration as a function of zonal-mean height. During summer, when CH_4 oxidation is faster, the total column values are 5–10% lower than in winter. CH_4 is removed in the troposphere and stratosphere by reaction with the hydroxyl (OH) radical. This is a major source of water in the stratosphere.

- About one-third of CH_4, that is, 225×10^{12} g C/year (225 Tg) of CH_4 emissions arise naturally at the surface via, for example, geological activity (Etiope and Klusman, 2002) or methanogenic bacteria under anaerobic conditions (wetlands and oceans) (Intergovernmental Panel on Climate Change, IPCC, 2001; Krüger *et al.*, 2001).
- The remaining two-thirds arise from human activity (industry and agriculture).
- Stratospheric CH_4 is rather inert, with a typical lifetime of 5–10 years, so it acts as a tracer of dynamical air motions.

This can be seen in Fig. 6, which shows contours curving upward (rising air) in the tropics and downward (sinking air) toward the pole. This is the so-called equator-to-pole circulation of the Earth, which will be discussed later. Mesospheric CH_4 is low due to stratospheric oxidation.

2.4. Nitrous oxide (N_2O)

Like CH_4, N_2O is most abundant in the troposphere. It is extremely inert with a lifetime of around 150 years and, hence, is a good indicator of dynamical motions.

- $7–14\times10^{12}$ g N/year N_2O are emitted into the atmosphere (Oonk and Kroeze, 1998), mainly via denitrifying bacteria.

In the stratosphere, about 95% N_2O is removed via photolysis in the stratosphere. The remaining 5% reacts with O^1D to form NO.

- A breakdown of N_2O contributes to O_3 destruction via NO_x cycles.

Little N_2O survives into the mesosphere, where concentrations are about 500 times less than they are in the stratosphere.

2.5. Atmospheric dynamics and temperature

On Earth, the total O_3 column is sensitive to atmospheric dynamics because a large amount of O_3 resides between 18–25 km, where chemical loss is slow. Other biomarkers occur mainly in the troposphere, where they are well mixed, so their column values are less sensitive to dynamical influence.

- Enhanced solar heating in the tropics coupled with Earth's rotation sets up an equator-to-pole flow called world circulation, meridional circulation, or Brewer-Dobson (Brewer, 1949) circulation (Holton, 2004).

On Earth, in a 10-year cycle, air enters the lower stratosphere in the tropics, travels up into the summer mesosphere, then back across the equator into the winter hemisphere, moving poleward and downward. The circulation is stimulated by atmospheric waves (Haynes, 1991), for example, gravity waves that can form when air flows over mountains or planetary

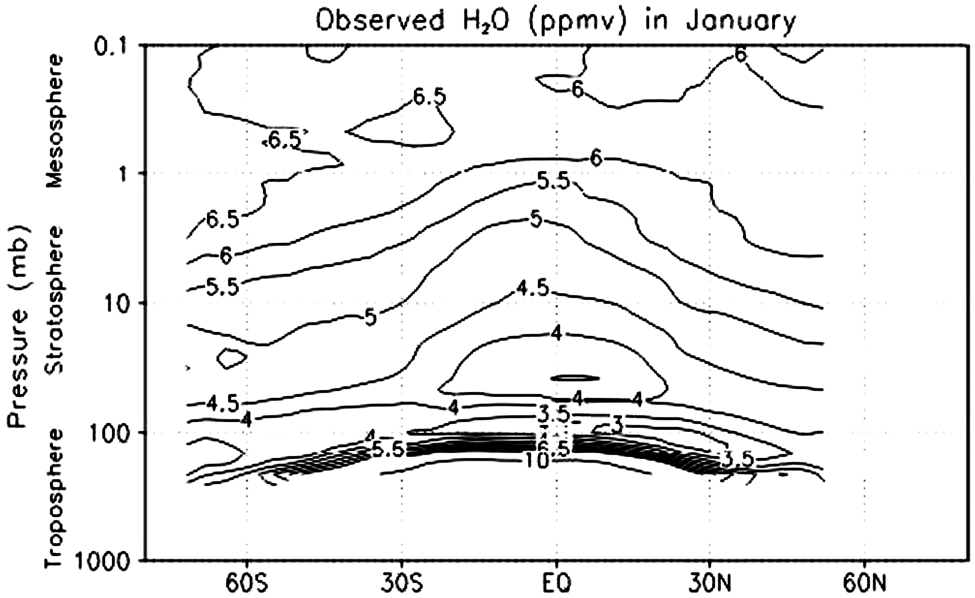

FIG. 5. As for Figure 4 but for water concentration in parts per million by volume shown in Earth's atmosphere as a function of zonal-mean height.

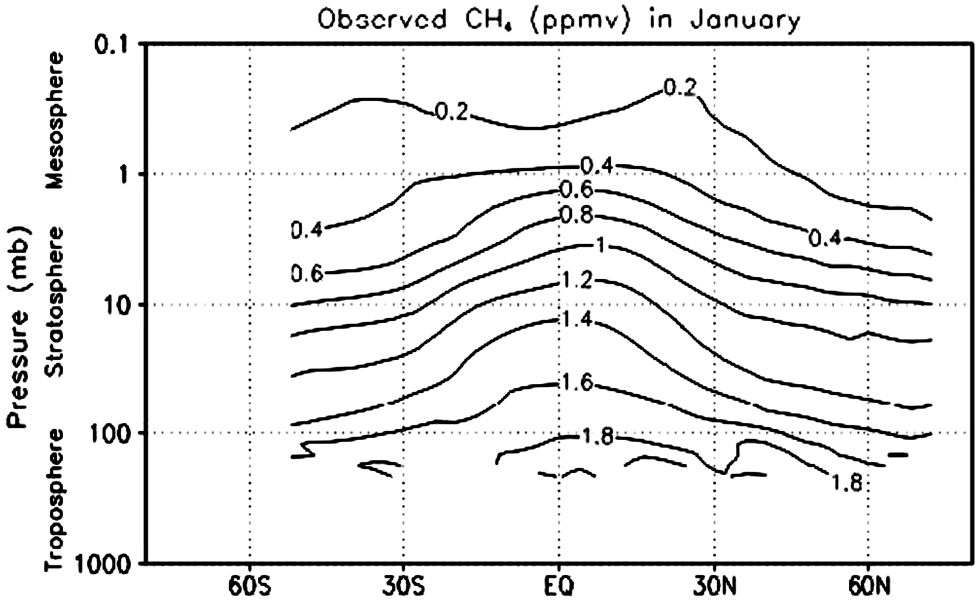

FIG. 6. As for Figure 4 but for methane concentration in parts per million by volume shown in Earth's atmosphere as a function of zonal-mean height.

waves which form via conservation of potential vortices when air moves in the north-south plane on a rotating globe.

Figure 7 (left) shows zonal-mean temperature in Kelvin as a function of altitude. Up to 100 mbar air cools due to adiabatic expansion. Above that height, radiative heating, mainly from O_3, leads to a temperature inversion and marks the start of the stratosphere. Between 1–0.1 mbar, this heating subsides, and cooling with height marks the start of the mesosphere.

3. Implications for Terrestrial Exoplanets

Earth's climate is nonlinear with complex feedbacks. It is therefore challenging for current climate models to reproduce accurately, for example, the O_3 response to climate change over the past 20 years (see the IPCC Third Assessment Report on Climate Change, 2001, for an overview). Several groups have investigated Earth's atmospheric evolution (Pavlov *et al.*, 2000; Kasting and Catling, 2003) from reducing (*i.e.*, non-oxidizing) atmospheres for which differing levels of CH_4 and CO_2 are assumed to the present-day atmosphere. Spectral modes of these evolution scenarios show different detectable features over Earth's geological history in low resolution (Kaltenegger *et al.*, 2007).

Ozone in the troposphere: sensitivity computational model runs for varying solar flux as well as CH_4, O_2, and NO_x concentrations appropriate to the Proterozoic period of early Earth indicated that the tropospheric O_3 column could sometimes constitute appreciably more than today's 10% of the total column (Grenfell *et al.*, 2006). The additional O_3 was produced via the photochemical smog mechanism, in which CH_4 oxidation is catalyzed by NO_x. The mechanism therefore favors terrestrial exoplanets with:

- weak stratospheric O_3, therefore high UV levels that reach the troposphere;
- abundant CH_4 from volcanoes, methanogens, or both; and
- abundant NO_x (from lightning and the action of cosmic rays on N_2/O_2 atmospheres).

Ozone photolysis effect: For Earth, the standard stratospheric Chapman chemistry analysis assumes both a rapid interconversion of O and O_3, and O in a steady state so that rate of O production equals rate of O loss, $j(O_2) = k(O)(O_3)$, $(O_3) = j(O_2)/(O)k$, where j and k are photolysis and reaction coefficients, respectively.

- For terrestrial exoplanets, these assumptions may not apply because the rate of O production and O loss depend, for example, on temperature and UV radiation; therefore, one has to apply in first steps a simpler approach.

The reaction $O + O_3 \rightarrow 2O_2$ quickly slows at low temperatures; therefore, one can assume a cold case, in which this reaction can be neglected. In such a case, O_3 is destroyed directly by $h\nu < 320$ nm but is formed when O_2 dissociates at $h\nu < 242$ nm (UVC). Therefore, under such conditions, an interesting quantity is the ratio, $R = [\text{UVB (280–315 nm)}/\text{UVC (100–280 nm)}]$.

- If, on a terrestrial exoplanet, the atmospheric radiative transport differs potentially from Earth-like conditions, then regions that have small R values would experience weak O_3 loss (from direct O_3 photolysis in the UVB) but strong O_3 formation (from O_2 photolysis hence O_3 formation in the UVC).

At the top of the atmosphere, R, is:

- $R = 2.31$ (Sun), $R = 2.98$ (K2V), and $R = 0.92$ (F2V) stars (Segura *et al.*, 2003).

More studies are required to explore this theme further and establish where, or if, such effects can be valid.

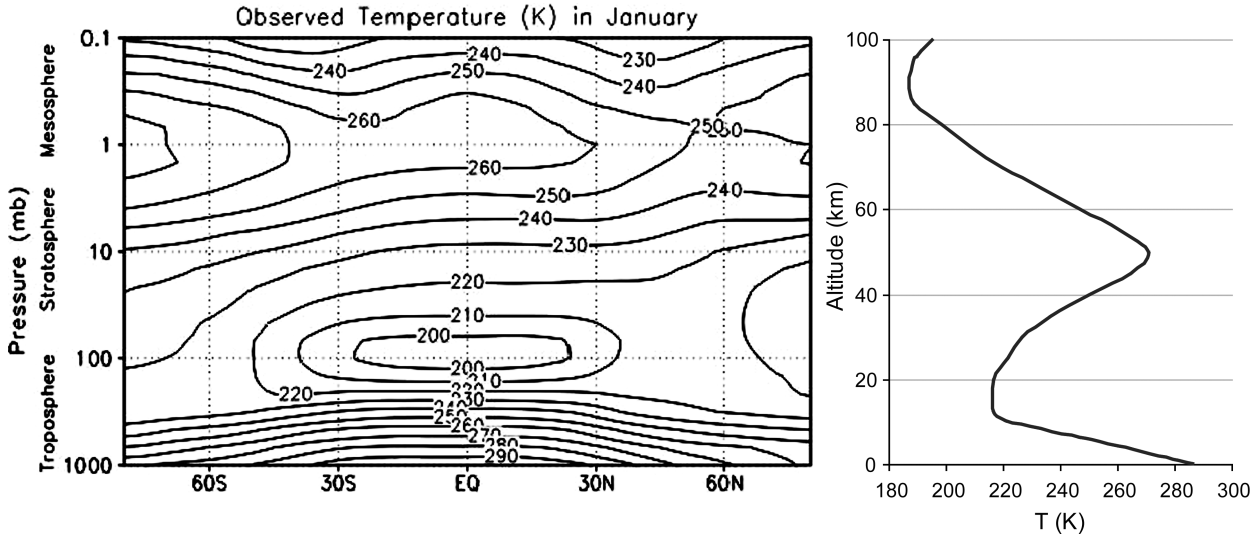

FIG. 7. Zonal-mean temperature (**left**) in Kelvin shown as a function of altitude. Data shows the mean January value from 1991 to 2002, derived from various observational platforms and compiled as part of the Stratospheric Processes and their Role in Climate Program by Bill Randel at the University Corporation for Atmospheric Research (Randel *et al.,* 2004). **Right:** average temperature profile of US1978 standard atmosphere.

Ozone temperature effect: That O_3 features a negative correlation with temperature has long been recognized (WMO, 1998). This behavior arises because the O_3 sink, $O + O_3 \rightarrow 2O_2$, speeds up considerably as temperature increases. The temperature dependency can be seen from the rate constant of the reaction, k, where $k = 8.0 \times 10^{-12} \exp^{(-2060/T)}$ (Sander *et al.,* 2003). Substituting $T = 200$, 250, 300 K implies $k = (2.7,\ 21.1,\ \text{and}\ 83.4) \times 10^{-16}$ molecules^{-1} cm^3 s^{-1}, respectively, that is,

- It can be expected that a large increase in the O_3 sink occurs as T increases.

This result is relevant to warm or hot exoplanets, for example, close to the inner edge of the habitable zone (HZ) or with strong greenhouse warming, or both.

Ozone and NO_x: Exoplanets in the HZ with M-dwarf hosts may have weak magnetospheres and, therefore, higher levels of cosmic ray bombardment. Grießmeier *et al.* (2005) suggested that the percent of cosmic rays that reach such a planet's surface be a factor of 2–10 greater, compared with Earth, assuming the two worlds have similar surface areas.

- Enhanced cosmic ray events imply increased atmospheric NO_x loadings because the cosmic ray particles can lead to ionization of N_2 (Siskind *et al.,* 1997).
- Such events on Earth typically lead to a 50–100% increase in NO_x in the upper stratosphere together with 10–30% O_3 loss (Jackman *et al.,* 2000; Quack *et al.,* 2001; Sinnhuber *et al.,* 2003).

The amount of total O_3 column loss depends on how easily NO_x can propagate down into the mid-stratosphere, where O_3 is most abundant.

Water and HO_x: Kasting *et al.* (1993) suggested that, near the inner edge of the HZ, all tropospheric H_2O may eventually overcome the tropopause cold trap and flood into the stratosphere.

- In such a scenario, destruction via HO_x cycles would then likely destroy most of the O_3 layer.

In general, this mechanism suggests that a temperature increase at the surface leads to faster evaporation and, hence, higher atmospheric humidity. The effect is difficult to quantify in climate models due to opposing mechanisms (*e.g.,* more H_2O leads to more clouds, which can produce a cooling effect) and interfering processes (*e.g.,* stratospheric H_2O also comes from CH_4 oxidation, the cold trap temperature is influenced by other factors) (IPCC, 2001). One can anticipate that ocean-world (Léger *et al.,* 2003) exoplanets are potentially most vulnerable to such a mechanism.

In addition to forming NO_x, cosmic rays may also lead to atmospheric HO_x formation. Solomon *et al.* (1981) suggested the mechanism for this, which involves an H_2O ion cluster. Similar to the NO_x effect discussed previously, the amount of total O_3 column loss depends on how easily HO_x can propagate down into the mid-stratosphere, where O_3 is most abundant.

- H_2O is particularly sensitive to Lyman-α (121.6 nm) radiation, whereby it rapidly photolyzes to form HO_x. Chandra *et al.* (1997) suggested 30–40% and 1–2% change in terrestrial H_2O at 80 km and 60 km, respectively, in response to Lyman-α changes.

Absolute Lyman-α fluxes are especially large for A stars (and, to a lesser extent, F stars). They are about 30 times larger during the first 100 Myr after G-type stars have arrived at the zero-age main sequence (Ribas *et al.,* 2005), so their exoplanets are the most likely candidates to lose their atmospheric H_2O via this mechanism, assuming a low-opacity atmosphere.

Ozone and dynamics: Terrestrial exoplanets with stronger differential heating gradients compared to those of Earth will feature a stronger equator-to-pole circulation.

- On Earth, for example, slowing this circulation would imply a change in the amount of O_3 found in the tropics (where it is formed) relative to the amount of O_3 at higher latitudes, to where it is transported. Other effects like strong temperature gradients would potentially influence such effects (Spiegel *et al.*, 2009).

Orographic features (mountains) also play an important role. On Earth, the Northern Hemisphere is much more mountainous than the Southern Hemisphere. Surface airflow over mountains leads to waves being excited, which carry heat and momentum up into the stratosphere and stimulate the equator-to-pole circulation, with the result that the Northern Hemisphere winter stratosphere is typically 10–20 K warmer than the Southern Hemisphere winter stratosphere (WMO, 1998). There is, however, no data for this effect over Earth's history, so the effect is difficult to quantify for different topologies. On a cloud-free planet with surface features like those of Earth, the diurnal flux variation in the visible caused by different surface features rotating in and out of view could be high, assuming hemispheric inhomogeneity (Ford *et al.*, 2001; Seager and Ford, 2002). When the planet is only partially illuminated, compared to a fully illuminated case, a more concentrated signal from surface features could be detected as they rotate in and out of view.

Methane (CH_4): Methanogen sources have quite specific temperature (and UV) dependencies that vary with species and environment (*e.g.*, soil type) (Nozhevnikova *et al.*, 2003). On early Earth, atmospheric sinks and geological sources may have been much stronger than they are today (Kasting and Catling, 2003); therefore,

- terrestrial exoplanets with fast tectonic activity and low O_2 may favor higher CH_4, while
- terrestrial exoplanets with some O_2 may favor fast CH_4 removal via OH.

Nitrous oxide (N_2O): N_2O is formed via denitrification in soil, which, like methanogenesis, is dependent on the temperature and the soil type (Li *et al.*, 1992).

- N_2O is destroyed mainly via UV radiation, which suggests that strong UV fluxes could lead to strong photolytic N_2O loss.

It is probably not useful to apply derived physical N_2O relationships to exoplanet conditions since responses (*e.g.*, of denitrifying bacteria) can be species specific and finely tuned to Earth conditions.

Biomarker molecules in Earth's atmosphere respond to complex feedbacks, which sometimes produce widely differing results, for example, in chemistry-climate model responses (IPCC, 2001). Nevertheless, it can be assumed that the main influences are sufficiently well known to justify a discussion of biomarkers on Earth-like exoplanets [see Kaltenegger *et al.*, 2010a (this volume)].

- O_3 is clearly sensitive to UV radiation in that it is both formed and destroyed in different regions of UV radiation, which depends on the radiative transfer in the atmosphere.
- Furthermore, O_3 concentrations are inversely proportional to temperature due to an increase in the sink: $O + O_3 \rightarrow 2O_2$. This will be especially important for terrestrial exoplanets near the inner HZ or with strong greenhouse warming.
- O_3 is destroyed catalytically by HO_x, ClO_x, and NO_x—the latter may be particularly important for terrestrial exoplanets orbiting the HZ of M and some K dwarfs.

Ultimately, more-sensitive computer simulations that use atmospheric models are required to separate out the influences of the various feedbacks. H_2O, CH_4, and N_2O present additional measurement difficulties since they mainly exist in the troposphere below the cloud base.

- Warming the troposphere leads to more H_2O overcoming the cold trap at the tropopause and hence reaching the stratosphere. If this process proceeds too quickly, it will lead to removal of the O_3 layer via HO_x destruction.

Estimating changes in CH_4 and N_2O sources on terrestrial exoplanets is difficult since, on Earth, they vary from organism to organism and are adapted to their particular biological niche.

- Regarding H_2O, CH_4, and N_2O sinks, enhanced stellar fluxes are expected to lead to a faster direct photolytic sink, as well as faster removal via $(CH_4 + OH)$ and $(N_2O + O^1D)$, since the radicals OH and O^1D are formed photolytically.

Regarding seasonal and diurnal chemical cycles, these are most easily detected for O_3 (again, because other biomarkers occur mainly in the troposphere, where photolysis rates are low). On Earth, O_3 column seasonal variations are in the region of about 20% for the natural cycle at midlatitudes and about 50% for human-induced O_3-hole variations poleward of about 60°.

- Clearly, in the case of terrestrial exoplanets, the strength of the biomarker seasonal signal will depend on the viewing geometry. Note that first-generation space missions will observe disk-integrated spectra of exoplanets with no spatial resolution.

If we view only one hemisphere, then the seasonal signal will be strong compared to instances where both hemispheres are viewed simultaneously. On Earth, a small seasonal O_3 signal still persists, even if we average data over both hemispheres. Austin (2002) suggested a 3% cycle in mean observed column O_3 (averaged from 65°S to 65°N, *i.e.*, excluding the effects of the man-made O_3 hole), with peak values in the Northern Hemisphere spring (which does not translate into a feature that is remotely detectable). This result is related to hemispheric asymmetry—the meridional circulation is stronger in the north due to more wave stimulation from mountain ranges.

However, it is entirely feasible that seasonal and daily biomarker amplitudes for many terrestrial exoplanets could be greater than those of Earth. Larger obliquity, for example, leads to stronger seasonal variations in stellar flux and temperature. Increases in ellipticity lead to seasons of unequal duration, as on Mars, and larger differences between closest and farthest approach also lead to large amplitudes in seasonal fluxes and temperatures.

Bertrand *et al.* (2002) and Williams and Pollard (2003) performed sensitivity runs for an Earth-like exoplanet with changed orbital parameters (*e.g.,* increasing ellipticity), using a climate model. The latter study suggested an intensely strong seasonality, for example, equatorial surface temperatures varying from zero in winter up to 80°C in summer that would potentially be a much stronger influence on chemical variation.

4. Conclusions

Studying biomarkers helps us understand the potential chemistry on exoplanets, different chemical cycles, as well as observed spectra. It is worth exploring the parameter space of biomarkers because we see only a very limited range here on Earth.

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Abbreviations

HZ, habitable zone; PAL, present atmospheric level.

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